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Expect the unexpected. Isolation and characterisation of some unusual organometallic gold(I) complexes

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This paper is dedicated to our mentor and friend Professor Martin Bennett on the occasion of his retirement for a lifetime contribution to organometallic chemistry

Abstract

The reaction of equimolar amounts of 2-Li-3-$MeC_6H_3PPh_2$ and [AuBr($AsPh_3$)] gives a mixture of the cyclometallated digold(I) complex [Au_2(μ-6-MeC_6H_3-2-PPh_2)$_2$] and the 'half-cyclometallated' complex [(Ph_3As)Au(μ-6-MeC_6H_3-2-PPh_2)AuBr] (**1**). This complex represents the first example of an intermediate of a cycloauration reaction that has been structurally characterised by X-ray diffraction. The reaction of [Au_2(μ-6-MeC_6H_3-2-PPh_2)$_2$] with mercuric chloride gives the unusual heteronuclear Hg(II)/Au(I) complex [ClHg(μ-6-MeC_6H_3-2-PPh_2)AuCl] (**2**), arising from electrophilic cleavage of a gold-carbon σ-bond, and not the oxidative addition product.

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1. Introduction

The element gold and its varied, interesting and often unusual chemistry have fascinated medieval alchemists and modern-day researchers alike. In recent years, gold chemistry has experienced a renaissance, evident in the appearance of hundreds of research papers and comprehensive monographs. A large number of gold containing structures have been reported over recent years, out of which several examples stand out: hypercoordinated complexes [$E(AuPPh_3)_n$]$^{m+}$ where E = C [1,2], N [3], O [4] and As [3], self-assembling macrocyclic singly- and doubly-braided [2]catenanes [5,6] and a large variety of homonuclear gold clusters. In our work we have continued to study the oxidative addition and reductive elimination chemistry of dinuclear cyclometallated gold(I) complexes of the type [Au_2(μ-$C_6H_4ER_2$)$_2$], where E = P, As and R = Et, Ph [7]; work that originated from Martin Bennett's group in Australia in the 1980s. The digold(I) complexes [Au_2(μ-$C_6H_4PR_2$)$_2$] undergo oxidative addition reactions with halogens to give metal-metal bonded digold(II) complexes which, on warming, rearrange to give carbon–carbon coupled products (Scheme 1), [7,8]. To further elucidate the mechanism leading to C–C coupling we have studied the analogous methyl substituted digold(I) complexes [Au_2(μ-*n*-MeC_6H_3-2-PPh_2)$_2$], where *n* = 5, 6. In comparison to the unsubstituted parent complex, the 6-methyl substituted digold(II) analogue displays quite different reactivity. Instead of rearranging to a C-C coupled product these digold(II) complexes very rapidly isomerise to heterovalent gold(I)/gold(III) complexes (Scheme 1), [9,10]. During the course of this investigation we have isolated and characterised two unusual and unexpected compounds, the structures of these will be presented here.

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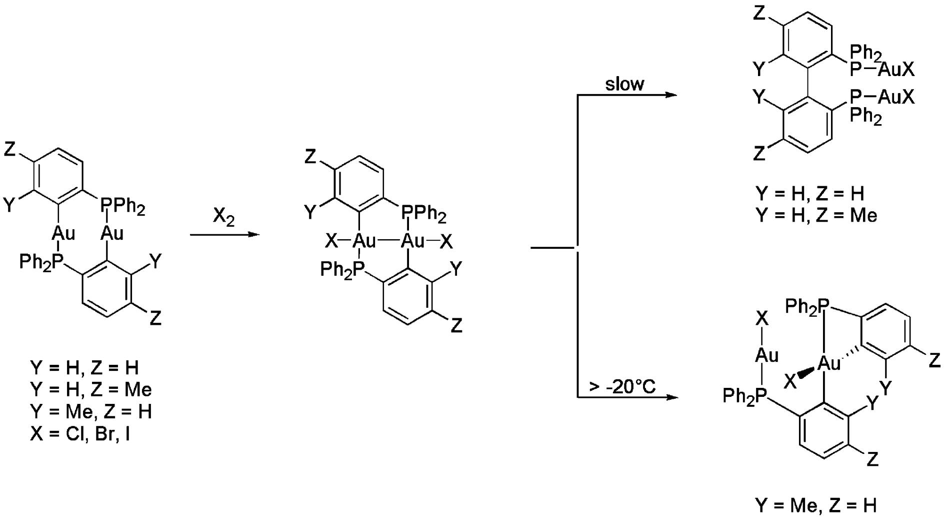


Scheme 1.

2. Experimental

2.1. General procedures

The syntheses were performed under dry argon with the use of standard Schlenk techniques, although the solid gold complexes, once isolated, were air-stable. Solvents were dried by standard methods, distilled, and stored under nitrogen. The following instruments were used for spectroscopic measurements: Varian Gemini 200 (^{1}H at 200 MHz), Bruker Aspect 2000 (^{31}P at 80.96 MHz), VG ZAB-2SEQ (EI mass spectra) and Perkin Elmer FT 1800 (IR spectra as polyethylene disks in the range 400–150 cm^{-1}). The NMR chemical shifts (δ) are given in ppm relative to TMS (^{1}H) and 85% H_3PO_4 (^{31}P), referenced either to residual solvent signals (^{1}H) or externally (^{31}P). Elemental analyses were performed by the Microanalytical Laboratory of the Research School of Chemistry at the Australian National University.

2.2. Syntheses

The starting materials 2-Br-3-MeC$_6$H$_3$PPh$_2$ [11], [AuBr(AsPh$_3$)] [12] and [Au$_2$(μ-6-MeC$_6$H$_3$-2-PPh$_2$)$_2$] [9] were prepared according to literature procedures.

2.2.1. [(Ph$_3$As)Au(μ-6-MeC$_6$H3-2-PPh$_2$)AuBr] (1)

A solution of ^{n}BuLi (2.25 ml of a 1.6 M solution in hexane, 3.6 mmol) was added dropwise to a solution of 2-Br-3-MeC$_6$H$_3$PPh$_2$ (1.17 g, 3.3 mmol) in a 1:1 mixture of ether and hexane at room temperature. The resulting precipitate of 2-Li-3-MeC$_6$H$_3$PPh$_2$ (0.649 g, 2.3 mmol) was washed by decantation with hexane and suspended in ether (25 ml). This was added to a stirred suspension of [AuBr(AsPh$_3$)] (1.34 g, 2.3 mmol) in ether (20 ml) at −78°. The mixture was stirred at this temperature for approximately 4 h then warmed to room temperature overnight. The supernatant was removed by decantation and the colourless solid washed with ether (3 × 10 ml), methanol (5 ml), hexane (15 ml) and dried in vacuo. The resulting greyish solid was then dissolved in dichloromethane (20 ml) and filtered through Celite. Concentration of the filtrate under reduced pressure and addition of hexane gave a colourless solid, which was isolated by filtration and dried in air. ^{31}P{^{1}H} NMR spectroscopy showed that the product consisted of approximately 50:50 mixture of **1** and [Au$_2$(μ-6-MeC$_6$H3-2-PPh$_2$)$_2$]. Crystals suitable for X-ray diffraction were obtained by slow evaporation from CH_2Cl_2/hexane. Data for **1**: ^{31}P{^{1}H} NMR (CDCl$_3$) δ 36.4 (s); ^{1}H NMR (CDCl$_3$) δ 2.7 (s, 3H, C*H*$_3$), 6.6–7.5 (m, 28H, Arom); IR (polyethylene disk, cm^{-1}) 235 (Au-Br).

2.2.2. [ClHg(μ-6-MeC$_6$H3-2-PPh$_2$)AuCl] (2)

To a solution of [Au$_2$(μ-6-MeC$_6$H3-2-PPh$_2$)$_2$] (200 mg, 0.21 mmol) in dichloromethane (20 ml) was added HgCl$_2$ (57 mg, 0.21 mmol) and stirred for 2 h. The solution was concentrated under reduced pressure to approximately 10 ml and hexane added to precipitate a colourless solid. This was isolated by filtration, washed with hexane and air-dried. The yield was 220 mg (71%). M.p.: 270° (dec); ^{31}P{^{1}H} NMR (CDCl$_3$) δ 41.9 ($^3J_{P-Hg}$ 392 Hz); ^{1}H NMR (CDCl$_3$) δ 2.6 (s, 3H, C*H*$_3$), 6.8–7.8 (m, 13H, Arom); EI–MS *m/z* 709 [M–Cl]$^+$, 507 [M-HgCl]$^+$, 471 [M–HgCl$_2$]$^+$; IR (polyethylene disk, cm^{-1}) 341.7 (Hg-Cl), 324.2 (Au–Cl); *Anal*. Found: C, 30.47; H, 2.27; P, 3.89 Calc. for $C_{19}H_{16}AuCl_2HgP$: C, 30.68; H, 2.17; P, 4.16. Crystals suitable for X-ray diffraction were obtained by layering the mother liquor with hexane.

2.3. Structure determinations

The structures were solved by direct methods (SIR 92) [13] (**1**) or heavy-atom Patterson methods [14] (**2**) and were expanded by the use of Fourier techniques [15]. Hydrogen atoms were included at geometrically determined positions, which were periodically recalculated but not refined. Methyl hydrogen atoms were oriented to best-fit peaks in difference electron density maps. The neutral atom scattering factors were taken from Ref. [16]; $\Delta f'$ and $\Delta f''$ values and mass attenuation coefficients were taken from Ref. [17]. Anomalous dispersion effects were included in F_{calc} [18]. All calculations were performed with the TEXSAN crystallographic software package [19]. The crystallographic details for complexes **1** and **2** are listed in Table 1.

3. Results and discussion

Reaction of equimolar quantities of 2-Li-3-$MeC_6H_3PPh_2$ with $[AuBr(AsPh_3)]$ gives a colourless solid, which shows two singlets of approximately equal intensity at δ 36.2 and 36.4 in the $^{31}P\ \{^1H\}$ NMR spectrum; the former peak corresponding to the cyclometallated gold(I) complex $[Au_2(\mu\text{-}6\text{-}MeC_6H3\text{-}2\text{-}PPh_2)_2]$ (Scheme 2). However, the identity of the second component could not be established. A crystal of this unknown compound was serendipitously selected and analysed by X-ray diffraction. This showed that the compound was the 'half-cyclometallated' complex $[(Ph_3As)Au(\mu\text{-}6\text{-}MeC_6H3\text{-}2\text{-}PPh_2)AuBr]$ (**1**) shown in Fig. 1; selected bond lengths and angles are listed in Table 2.

The compound consists of two linearly coordinated gold(I) atoms bridged by one molecule of the 6-$MeC_6H_3PPh_2$ ligand through gold-carbon and gold-phosphorus bonds. In addition, one gold atom is bonded to bromide and the other coordinated to $AsPh_3$. The Au-Br distance 2.394(2) Å is similar to that in $[AuBr(AsPh_3)]$ [2.377(6) Å] [20] and in $[AuBr(PPh_3)]$ [2.252(6) Å] [21]. The Au–As distance 2.390(2) Å is slightly greater than that of $[AuBr(AsPh_3)]$ [2.342(5) Å], consistent with the higher *trans*-influence of the σ-aryl group. The Au-P and Au-C distances [2.245(3) and 2.07(1) Å, respectively] are similar to those in $[AuPh(PPh_3)]$ [Au–P 2.296(2) Å and Au-C 2.045(6) Å] [22].

Table 1
Crystallographic data for compounds **1** and **2**

	1	**2**$\cdot 1/2HgCl_2$
Formula	$C_{37}H_{31}AsAuBrP$	$C_{19}H_{16}AuCl_3Hg_{1.5}P$
Formula weight	1055.38	879.52
Space group	$P2_1/c$	$C2/c$
a (Å)	8.958(2)	27.277(3)
b (Å)	15.511(2)	11.133(3)
c (Å)	25.032(1)	17.882(4)
β (°)	96.33(1)	125.83(1)
V (Å^3)	3456.9(9)	4402(2)
Z	4	8
ρ_{calc} (g cm^{-3})	2.028	2.654
μ (cm^{-1})	184.91	175.82
R [a]	0.042	0.036
R_w [b]	0.043	0.033

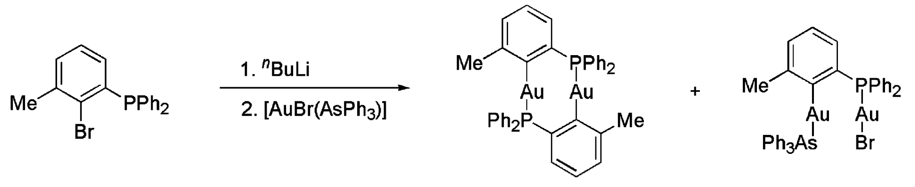
[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2}$, where $w = 1/[\sigma^2(F_o)]$.

Complex **1** represents the first example of an intermediate in a cycloauration reaction involving P-donor ligands that has been structurally characterised by X-ray diffraction. It is evident that a further molecule of 2-Li-3-$MeC_6H_3PPh_2$ can displace the bromide to form a second gold-carbon σ-bond with loss of LiBr. In a subsequent (or simultaneous) step, the phosphorus atom displaces the triphenylarsine to form the second Au-P bond and thus yield the fully cyclometallated product. This suggests complex **1** is an intermediate in the cycloauration reaction rather than merely a by-product. Despite numerous attempts at developing a rational synthesis for this complex, we have been unsuccessful so far. It is noteworthy that analogous intermediates have neither been observed nor isolated when phosphine gold(I) precursors such as $[AuBr(PPh_3)]$ and $[AuBr(PEt_3)]$ were used in the reaction. It may be that these 'half-cyclometallated' complexes normally react very quickly to form the fully cycloaurated products and that, for some unknown reason, we have been lucky to isolate this product before it could react any further.

Very few other reports of any intermediates involved in cycloauration reactions have appeared in the literature. The C-coordinated 2-pyridyl complex $[Au(2\text{-}C_5H_4N)(AsPh_3)]$ has been postulated as an intermediate in the cyclometallation reaction of $2\text{-}LiC_5H_4N$ with $[AuCl(AsPh_3)]$ to give the trinuclear complex $[Au_3(\mu\text{-}C_5H_4N)_3]$ [23]. However, the structure of this intermediate has not been confirmed by X-ray crystallography.

Mercuric chloride reacts with low oxidation state transition metal complexes resulting in products with a variety of possible structures: both chlorides can be displaced to give metal–mercury–metal bonds [24], only one chloride can be displaced to give M-HgCl compounds [25,26] and in addition, $HgCl_2$ can form simple metal adducts [27,28] or form bridges between two metals [29]. It was therefore expected that mercuric chloride would oxidatively add to the digold(I) complex resulting in the formation of a Cl-Hg-Au-Au-Cl unit. However, the reaction of $[Au_2(\mu\text{-}6\text{-}MeC_6H3\text{-}2\text{-}PPh_2)_2]$ with $HgCl_2$ gives a colourless solid (Scheme 3), which shows a singlet at δ 41.9 in the $^{31}P\{^1H\}$ NMR spectrum with ^{199}Hg satellites ($^3J_{Hg-P} = 392$ Hz), inconsistent with the expected oxidative addition product structure.



Scheme 2.

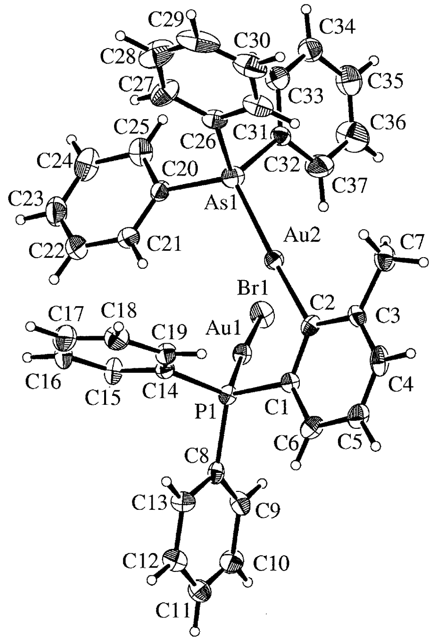


Fig. 1. Molecular structure of complex **1**. Ellipsoids show 30% probability levels. Hydrogen atoms are drawn as circles with small, arbitrary radii.

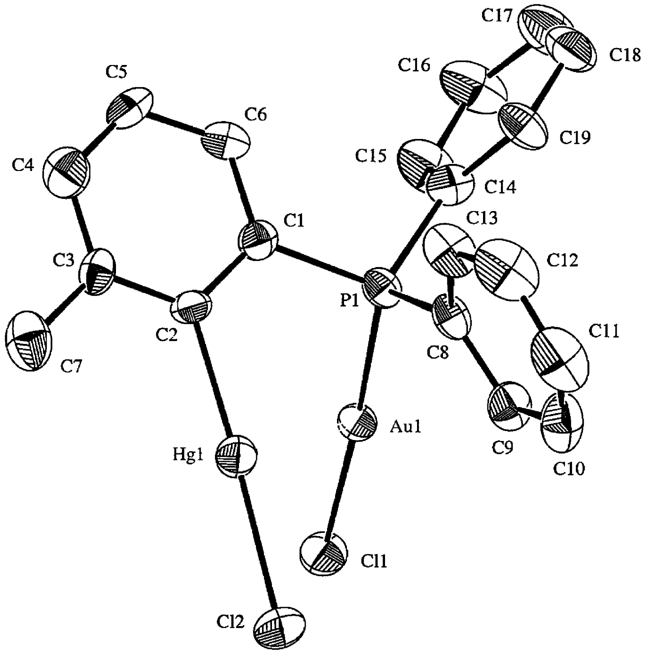


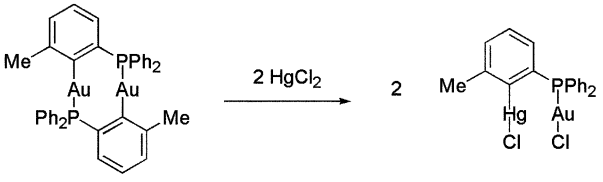
Fig. 2. Molecular structure of complex **2**. Ellipsoids show 30% probability levels. Hydrogen atoms and the co-crystallised $HgCl_2$ have been omitted for clarity.

Table 2
Selected bond distances (Å) and angles (°) in complex **1**

Au(1)···Au(2)	3.0927(8)	Au(1)–P(1)	2.245(3)
Au(2)–C(2)	2.07(1)	Au(1)–Br(1)	2.394(2)
Au(2)–As(1)	2.390(2)	As(1)–Au(2)–C(2)	173.0(3)
P(1)–Au(1)–Br(1)	176.5(1)	Au(1)–P(1)–C(1)	110.3(4)

Table 3
Selected bond distances (Å) and angles (°) in complex **2**

Au(1)···Hg(1)	3.2940(9)	Hg(1)–C(1)	2.07(1)
Hg(1)–Cl(2)	2.270(6)	Au(1)–P(1)	2.233(4)
Au(1)–Cl(1)	2.280(4)	Cl(2)–Hg(1)–C(2)	176.5(1)
Cl(1)–Au(1)–P(1)	176.1(2)	Au(1)–P(1)–C(1)	109.1(5)



Scheme 3.

The X-ray crystal structure (Fig. 2) shows that the product is in fact the heteronuclear Au(I)/Hg(II) complex [ClHg(μ-6-MeC$_6$H3-2-PPh$_2$)AuCl] (**2**), which also contains half a molecule of co-crystallised $HgCl_2$. Table 3 lists important bond lengths and angles. A similar compound has been obtained from the reaction of $[Au_2(\mu\text{-}C_6H_4PPh_2)_2]$ with $HgCl_2$ [30]. The structure of **2** consists of linearly coordinated Hg(II) and Au(I) atoms bonded to chloride atoms and bridged by a 3-$MeC_6H_3PPh_2$ unit. The Au-Hg distance of 3.2940(9) Å is significantly longer than that in the non-methylated analogue [3.112(1) Å] [30], indicative of very little or no metal–metal interaction. The Hg-C and Hg-Cl distances [2.07(1) and 2.270(6) Å, respectively] in **2** are very similar to those observed in [HgClPh] [Hg–C 2.044(9) Å and Hg–Cl 2.345(2) Å] [31]. Furthermore, the Au–P and Au-Cl distances [2.233(4) and 2.280(4) Å, respectively] are identical (within experimental error) to those in $[AuCl(PPh_3)]$ [32]. Complex **2** is formed by electrophilic cleavage of the σ-aryl carbon–metal bond by $HgCl_2$, which is a well-established class of reaction.

4. Conclusions

Serendipitously we have, for the first time, isolated and structurally characterised an intermediate of a cyclometallation reaction. Repeated attempts to rationally prepare this complex have, so far, been unsuccessful, with the proposed intermediate reacting rapidly, giving the fully cycloaurated product. Mercuric chloride is known to react with transition metal complexes, giving a variety of possible structures. In this case electrophilic cleavage of gold-carbon σ-bonds occurs and a heteronuclear Hg(II)/Au(I) complex is formed.

5. Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 172010 and 172011. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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